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TITLE: HEAT RESISTANT FERRITIC STAINLESS STEEL

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INVENTOR-INFORMATION:

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INT-CL (IPC): C22C 38/00; C22C 38/50; C22C 38/54

ABSTRACT:

PURPOSE: To produce a ferritic stainless steel having excellent high temp. strength and thermal fatigue resistance particularly at 600-650°C exhaust gas temp. as compared with the conventional steel such as SUH409, also having oxidation resistance up to $\leq 800^{\circ}\text{C}$ and superior workability and corrosion resistance in a weld zone and toughness, and suitably used as automobile exhaust system member or exhaust gas passage member for LNG/thermal compound power generation.

CONSTITUTION: This heat resistant ferritic stainless steel has a composition consisting of, by weight, $\leq 0.015\%$ C, $0.2-0.8\%$ Si, $0.2-0.8\%$ Mn, $\leq 0.03\%$ P, $\leq 0.002\%$ S, $11-14\%$ Cr, $\leq 0.5\%$ Ni, $>0.2-0.5\%$ Nb, $0.06-0.2\%$ Ti, $\leq 0.015\%$ N, $0-0.2\%$ Al, and the balance Fe with inevitable impurities, further containing, if necessary, one or ≥ 2 kinds among $0.3-2\%$ Mo, $0.1-1\%$ W, $0.1-0.5\%$ V, and $0.0003-0.005\%$ B, satisfying $\text{C+N} \leq 0.02\%$ and $(\text{Nb+Ti})/(\text{C+N}) \geq 20$, and also satisfying $\text{Al} \geq 2\text{N}$ when Al is contained.

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(54) 【発明の名称】 耐熱フェライトステンレス鋼

(57) 【要約】

【目的】 SUH409等の従来鋼に比べ、特に排ガス温度600～650℃にて優れた高温強度、耐熱疲労性を有し、800℃までの耐酸化性と、優れた加工性と溶接部耐食性、靱性を有した自動車排気系部材あるいはLNG火力複合発電の排ガス経路部材として適したフェライトステンレス鋼を得ることを目的とする。

【構成】 重量%で、C:0.015%以下、Si:0.2～0.8%未満、Mn:0.2～0.8%未満、P:0.03%以下、S:0.002%以下、Cr:11～14%、Ni:0.5%以下、Nb:0.2%を超え0.5%以下、Ti:0.06～0.2%、N:0.015%以下、Al:0～0.2%、及び必要により、Mo:0.3～2%、W:0.1～1%、V:0.1～0.5%、B:0.0003～0.005%以下のうち1種または2種以上含み、かつC+N≤0.02%、(Nb+Ti)/(C+N)≥20、及びAlを含有する場合はAl≥2Nを満足し、残部がFeおよび不可避免的不純物からなる耐熱フェライトステンレス鋼。

【特許請求の範囲】

【請求項1】重量%で、C:0.015%以下、Si:0.2~0.8%未満、Mn:0.2~0.8%未満、P:0.03%以下、S:0.002%以下、Cr:11~14%、Ni:0.5%以下、Nb:0.2%を超え0.5%以下、Ti:0.06~0.2%、N:0.015%以下、Al:0~0.2%、を含有し、かつ $C+N \leq 0.02\%$ 、 $(Nb+Ti)/(C+N) \geq 20$ 、及びAlを含む場合は $Al \geq 2N$ を満足し、残部がFeおよび不可避的不純物からなる耐熱フェライトステンレス鋼。

【請求項2】さらに、Mo:0.3~2%、W:0.1~1%、V:0.1~0.5%、B:0.0003~0.005%以下のうち1種または2種以上含むことを特徴とする請求項1記載の耐熱フェライトステンレス鋼

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、各種内燃機関の排ガス経路部材として好適な耐熱フェライトステンレス鋼に関する。例えば、自動車排気系部材や、排熱回収ボイラ

【0002】

【従来の技術】自動車排気マニホールド、フロントパイプ、センターパイプ（以下自動車排気系管という）等の排気系部材は、エンジンから排出される高温の燃焼ガスと接触する部位にあり、これを構成する材料には優れた加工性と、耐酸化性、高温強度、耐熱疲労性等、多様な特性が要求される。しかし、近年の排ガス規制の強化、さらには自動車のエンジン性能の向上による排ガス温度の上昇、車体計量化による燃費向上の要請等に応えるため、ステンレス鋼の溶接管が排気系材料として使用されるようになってきた。

【0003】一方、火力発電プラントにおいては、近年、排熱回収ボイラを用いた複合発電が盛んに行われ、発電用タービンの燃焼温度は上昇する傾向にあり、特にLNGを燃料とすることから、従来の1100℃級より、1300℃級、1350℃級が実際に計画、設置されるようになりつつある。それにともない、タービン出側の高温排ガスの熱を回収する排熱回収ボイラも高温化する傾向にある。例えば従来、550℃前後であった排ガス温度が100℃程度上昇し650℃前後になってきている。

【0004】オーステナイト系ステンレス鋼は、優れた耐熱性および加工性、溶接性を有している。代表的な鋼種としてはSUS304(18Cr-8Ni)、SUS310S(25Cr-20Ni)などがある。しかし、オーステナイト系ステンレス鋼は熱膨張係数が大きく、自動車排気管のような激しい加熱-冷却の繰返しを受ける用途においては、熱歪みに起因する熱疲労によって破壊が生じやすい。

【0005】また、LNG火力複合発電の排熱回収ボイラは、真夏等の消費電力ピーク期を除いて、一般的には昼間運転-夜間停止の操業方式をとる。よって、排熱経路部材のなかで、例えば内張りダクト等に、オーステナイトステンレス鋼を使用すると、熱膨張係数が大きいことから熱歪みによる変形等の危険がある。

【0006】一方、フェライト系ステンレス鋼は、オーステナイト系ステンレス鋼より熱膨張係数が小さいため、こうした熱歪みによる疲労破壊や変形が回避でき、また安価であるからフェライト系ステンレス鋼の方が自動車排気管や内張りダクト等に用いる場合に有利となる。

【0007】600℃以上における耐熱性、特にクリープ強度の面ではフェライトステンレス鋼は、オーステナイトステンレス鋼に及ぶべくもないが、前述のように、熱膨張係数が小さいこと、安価であるといった利点を活かして、それほどクリープ強度が要求されない構造部材に適しているといえる。従来、耐熱フェライトステンレス鋼としては、一般にSUH409L(12Cr-Ti)が用いられてきた。しかし、自動車排気系、排熱回収ボイラの排ガス温度の上昇と共に、さらに高温強度、クリープ強度に優れた材料が望まれていた。

【0008】さらに、LNG火力複合発電の排熱回収ボイラの排ガス中には10%程度の水分と5%程度の炭酸ガスが含まれ、これらの凝縮水による運転停止時の露点腐食が懸念されており、特に溶接部での耐食性改善が望まれていた。

【0009】特開昭60-145359号公報には、「C:0.05%以下、Si:1.0~2.0%、Mn:2%以下、Cr:6~25%、Mo:5%以下（ただし、 $Cr+Mo \geq 8\%$ ）、N:0.05%以下、Al:0.5%以下、Ti、Zr、Ta、Nbの1種以上（ただし、Ti、Zr、Ta、Nb量はすべてのC、Nを炭化物、窒化物とするのに必要な化学量論量）を含み、Nb:0.3%以下でしかも0.1%以上（好ましくは0.2%以上）の不結合（固溶）Nbからなる、周期的酸化抵抗とクリープ強さを有する高温用フェライト鋼」が開示されている。

【0010】同公報では周期的酸化抵抗にはSiの添加が有効であり、クリープ強度には、0.1%以上（好ましくは0.2%以上）の不結合（固溶）Nbの存在とSiに富むラーベス相の形成が重要であると述べられている。

【0011】しかしながら、本発明者らが上記フェライト鋼について検討した結果、1%以上のSiを含有させた場合、良好な母材靱性を得ることは容易ではなく、高温使用中に析出するラーベス相により脆化し、降温時に小さな衝撃で壊れる危険がある。特に、板厚3~9mmといった中厚板を構造部材として使用する場合、長時間使用時の信頼性が得られないということが判明した。また、この発明の実施例に開示されている鋼は、C、Nの安定化に寄与するNb、Ti量が少なく、溶接熱影響部

の粒界腐食を防止するには不十分であるという問題がある。

【0012】特公昭62-14626号公報には、鋼中S、Oを0.008%未満とし、鋼中介在物が高温でMnSより安定な介在物であることを特徴とした耐高温酸化性に優れたフェライト鋼が開示されている。

【0013】不純物であるS、Oの含有量を低減することにより、耐酸化性に悪影響を及ぼす介在物であるMnSあるいはCr、Si、Al、Mn等の酸硫化物の生成を抑えることを特徴としており、高温使用時あるいは溶接部のCr炭化物生成による耐酸化性の劣化を抑制するために、C固定元素としてTi、Nb、Zr、Taの1種または2種以上を合計でC量の4倍以上、1.5%以下の範囲で添加することが記載されている。

【0014】しかし、不純物のNについての検討がなされていなく、Nは母材及び溶接部の靱性に及ぼす影響が大きいと、なかでも溶接部の靱性に不安が残る。また、高温強度、熱疲労寿命に及ぼす諸元素の影響に関する検討が充分なされていない。

【0015】特に、C、N固定元素であるTi、Nb、Ta、Zrを2種添加した場合、NbとTiを複合添加した場合における加工性、成形性、靱性、高温強度、耐食性のバランスを考えた適正添加量に関する検討がなされていない。

【0016】

【発明が解決しようとする課題】本発明は、SUH409等の従来鋼に比べ、特に排ガス温度600~650℃にて優れた高温強度、耐熱疲労性を有し、800℃までの耐酸化性と、優れた加工性と溶接部耐食性、靱性を有した自動車排気系部材あるいはLNG火力複合発電の排ガス経路部材として適したフェライトステンレス鋼を得ることを目的とする。また、ユーザーの低コスト化にも対応できる安価なフェライトステンレス鋼材、例えば、自動車排気系において排気マニホールド・フロント・センターパイプ・マフラーに至る材料の一元化に寄与する材料の提供にある。

【0017】

【課題を解決するための手段】自動車排気系部材は一般に、板厚2mm以下の薄板あるいは溶接管であり、排熱回収ボイラダクト材の板厚としては1.5~6mmが主体で、9mm程度までの中厚板も使用される。いずれも構造上必要な耐酸化性、高温強度、耐熱疲労特性、加工性、靱性、溶接性が要求される。しかし、厳しい内圧等を受けない部材であるためSUS304や2.25Cr-1Moフェライト鋼並みのクリープ強度は要求されず、長期の使用に耐え得る高温強度を具備していれば良い。

【0018】そこで、本発明者らは従来鋼に比べ上記諸特性がより優れたフェライト鋼を開発すべく、鋭意研究を行った結果、下記のような知見を得るに至った。

【0019】A) Nbと0.006~0.2%の極狭い範囲の

Tiとを複合添加効果した場合に形成される(Nb、Ti)炭化物は、NbあるいはTi単独添加系における炭化物よりも高温で析出し、微細に析出するTiNを核として析出し易いのでその周辺には固溶C、Nの存在しない領域(Interstitial Free)が形成されるので、それにより軟質となり良好な加工性、成形性が得られるが、同時にラーベス相が優先析出するサイトが減少し、高温使用中におけるラーベス相の析出遅延に有効で、脆化を遅らせることができ、さらに、再結晶温度も低下させるので、熱歪みを緩和し熱疲労特性が向上すること。

【0020】B) $(Nb+Ti)/(C+N) \geq 20$ と規制することにより、母材及び溶接熱影響部の靱性が向上すると共に、凝縮水環境における溶接部の粒界腐食が防止されること。

【0021】C) 耐酸化性、靱性を向上させるために添加するAl量は、0.02%以上、 $Al \geq 2N$ とすることで熱延板及び熱影響部での靱性が向上すること。

【0022】本発明は、このような知見に基づき完成されたもので、その要旨は、「重量%で、C:0.015%以下、Si:0.2~0.8%未満、Mn:0.2~0.8%未満、P:0.03%以下、S:0.002%以下、Cr:11~14%、Ni:0.5%以下、Nb:0.2%を超え0.5%以下、Ti:0.06~0.2%、N:0.015%以下、Al:0~0.2%、及び必要により、Mo:0.3~2%、W:0.1~1%、V:0.1~0.5%、B:0.0003~0.005%以下のうち1種または2種以上含み、かつ $C+N \leq 0.02\%$ 、 $(Nb+Ti)/(C+N) \geq 20$ 、及びAlを含む場合は $Al \geq 2N$ を満足し、残部がFeおよび不可避的不純物からなる耐熱フェライトステンレス鋼」にある。

【0023】

【作用】次に、本発明鋼の合金成分および不純物に関して、含有量と作用について説明する。

【0024】CおよびN: C、Nの増加は、強度を向上させるが、靱性を劣化させ、加工性、溶接性に悪影響をおよぼす。したがって、C、Nはできるだけ低いことが望ましく、このためC:0.015%以下、N:0.015%以下とし、かつ $C+N \leq 0.02\%$ とする。望ましくはC:0.01%以下、N:0.010%以下、 $C+N:0.015\%$ 以下である。

【0025】 $C+N$ が0.03%を超えるとTi、Nbを複合添加しても充分C、Nを固定することができなく前記悪影響がでると共に、溶接部の粒界腐食感受性が高くなる。

【0026】Si: Siは、有効な脱酸元素であり、また耐酸化性に必須な元素である。0.2%以上の添加で耐酸化性向上に効果を発揮する。また、Siには、高温強度を向上させ、耐熱疲労特性を向上させる効果がある。これは、高温(>600℃)で析出するラーベス相(主に Fe_2Nb)において、Nbの一部をSiが置換する

ことにより、高温強度に寄与する固溶Nbの低下を抑えて、高温強度を保持するためである。0.8%以上添加すると、靱性、加工性を劣化させるので、Siは0.2~0.8%未満と狭い範囲とする必要がある。望ましくは0.2~0.6%である。

【0027】Mn:Mnは、脱酸元素であり、熱間加工性を向上する元素として知られる。しかし、MnSを形成し酸化の起点となったり、オーステナイト形成元素であることから、耐酸化性にとって好ましくない。よって、0.2~0.8%未満とした。望ましくは0.3~0.7% 10

【0028】Cr:耐酸化性及び耐食性に必須な元素である。11%未満ではその効果が現れず、14%を超えて添加すると、靱性、加工性を劣化させるため、上限を14%とした。

【0029】P:Pは、製造上の不可避的不純物の一つであるが、靱性、加工性への悪影響を避けるためには0.03%以下とする必要がある。

【0030】S:Sもまた製造上の不可避的不純物であるが、S量が多いとMnと同様、耐酸化性の点から好ましくなく、また溶接性にも悪影響を与えるので、上限を0.002%とする必要がある。 20

【0031】Nb:Nbは、フェライトステンレス鋼の弱点である高温強度、クリープ強度を向上させるうえで必須の元素であり、500℃以上でその効果が顕著に現れる。Nbは炭化物としてC、Nを固定する作用がある。本発明では、Nb:0.2%を超え、0.5%以下、 $C+N \leq 0.02\%$ としているため、 $\%Nb / (\%C + \%N) \geq 10$ となる。これにより、十分な高温強度、クリープ強度を得るのに必要な固溶Nb量を確保した。Nb量は、 30

高温強度の点から多いほど望ましいが、0.2%以下では十分な高温強度が得られず、0.5%を超えて含有するとラーベス相の析出が顕著になり、靱性が劣化することから、0.2%を超え、0.5%以下とした。

【0032】高温使用中(>600℃)にラーベス相(Fe_2Nb)が析出し、固溶Nb量の低下による高温強度の低下が起こるが、析出後にも十分な高温強度を得るには固溶Nb量として0.1%以上必要で、そのため0.3%を越えたNb量が必要であることを見いだした。また、ラーベス相析出による脆化の点からは極力Nb量は低い 40

ほど、トータルのラーベス相析出量が減少するので、好ましい上限は0.4%である。

【0033】Ti:Tiは、Nbと同様にC、Nの固定元素として有効である。特に、溶接熱影響部においてCr炭化物の生成を抑制し、靱性、耐食性の確保には不可欠な元素である。また、Ti、Nbには母材及び溶接熱影響部の結晶粒粗大化抑制効果を有する。これらの効果を十分に発揮させるには、 $(Nb+Ti) / (C+N) \geq 20$ 必要とする。望ましくは、これらの効果をさらに 50

2以上1.0以下とするのがよい。

【0034】NbとTiの複合添加した場合には、主としてTiはNと結合して窒化物を形成し、Nbと残りのTiはCと結合し、(Nb、Ti)炭化物を形成する。前記したように(Nb、Ti)炭化物は、NbあるいはTi単独添加系における炭化物よりも高温で析出し、微細に析出するTiNを核として析出し易い。よってその周辺には固溶C、Nの存在しない領域(Interstitial Free)が形成される。

【0035】これにより軟質となり良好な加工性、成形性が得られるが、同時にラーベス相が優先析出するサイトが減少し、高温使用中におけるラーベス相の析出遅延に有効で、脆化を遅らせることができる。さらに、再結晶温度も低下させるので、熱歪みを緩和し熱疲労特性が向上する。

【0036】以上の効果を発揮させる目的からTiは0.06%以上の含有が必要で、Nの4倍以上を確保しかつ若干の炭化物形成可能な量の下限である。0.2%を超える添加は、上記効果を向上させることはほとんどなく、圧延時の表面疵が顕著となることから上限は0.2%とした。

【0037】Ni:Niは製造上の不可避的不純物の一つである。微量のNiの添加は、靱性改善に有効であるが、耐酸化性に悪影響を及ぼすことから特に0.5%以下とした。

【0038】Al:Alは任意添加元素であり、脱酸元素として知られTiと共存するとその効果はより顕著となる。また、少量のAl添加により靱性が向上することが知られている。特に $2\%N \leq \%Al$ とすることで熱延板及び溶接熱影響部の靱性が向上する。溶接時においてはTiとともにNの固定に作用するため、その必要量は $2\%N \leq \%Al$ である。

【0039】また、0.02%以上のAl含有により耐酸化性が向上する。特に、Alが内部酸化してスケールに対し“くさび”の役割をする事で酸化スケールの耐剥離性を向上させて耐酸化性が向上する。これにより、排ガス中への酸化スケールの混入が抑制される。さらに、0.02%以上のAlは高温強度及びクリープ強度改善効果も有する。しかし、過剰の添加は、耐酸化性、高温強度への効果が飽和し、加工性へ悪影響を及ぼすため、上限を0.2%とした。

【0040】Mo:Moは任意添加元素であり、Nbと同様、高温強度を向上させる元素として知られる。MoはNbと異なり、高温使用中にラーベス相(Fe_2Mo)形成傾向が Fe_2Nb より小さく、長期にわたって固溶状態を保持するため固溶強化作用が持続される。よって、クリープ強度及び耐食性を改善にはMo添加が好ましい。この場合0.3%以下ではそれらの効果が十分でないため、下限を0.3%とした。しかし、過剰の添加は、靱性、加工性を低下させる。さらにコスト高となる

ため、添加する場合は上限を2.0%とした。

【0041】W: Wは任意添加元素であり、Nb、Moと同様高温強度を向上させる元素として知られる。WもMoよりも更にラーベス相の形成傾向が小さく、固溶強化作用ががより長期にわたり持続されるため、クリープ強度が向上する。0.1%以下ではその効果が十分でなく、過剰の添加は、靱性、加工性を劣化させ、コスト高となるため0.1~1%とした。

【0042】V: Vは任意添加元素であり、固溶状態あるいは炭窒化物を形成して高温強度を向上させると共に、加工性を改善する。0.1%以上でその効果が現れる。しかし、0.5%を超えて含有させると返って加工性を低下させるので、0.1~0.5%とした。

【0043】B: Bは任意添加元素であり、高温強度、耐酸化性を改善する目的で含有させる。

【0044】その改善効果が現れる理由は定かではないが、Bは一般的に粒界に偏析しやすい元素として知られているので、粒界すべりを阻止して高温強度を改善するものと考えられる。また、粒界偏析により、耐酸化性に有害なP、S等の不純物元素を排出して、耐酸化性を向上させるものと考えられる。この効果は0.0003%以上で現れ、0.005%を超えて含有させると靱性、加工性も劣化させるので0.0003~0.005%とした。

【0045】

【実施例】まず、表1に示される組成を有する鋼を、溶*

*解、鍛造後、加熱温度1150℃にて熱間圧延を行い、板厚4.5mmに仕上げ、960℃にて焼鈍して熱延板を作製した。さらに、4.5mm厚の熱延板に冷間圧延を施し、960℃にて仕上げ焼鈍を行って、板厚1.5mmの冷延板を作製した。冷延鋼板からは、T方向からJIS 13B号の厚さ1.5mmの常温引張試験片及び厚さ1.5mm、幅20mm、長さ25mmの酸化試験片を採取した。冷延板を電縫溶接により製管して熱疲労試験片を作製した。

10 【0046】図1は、熱疲労試験片の形状を示す図で、1が試験材の管で、2か所に径8mmの穴(2、3)を明け、冷却用エアの供給口3となっている。4は管の内面からの保持具(芯金)、5は試験機のホルダーへの取り付け部である。管1と保持具4は固定用ピン6と端部の溶接部7によって固定されている。

【0047】熱疲労試験には、コンピュータ制御の電気油圧サーボ式高温熱疲労試験装置を用い、試験は図2に示す温度サイクル及び機械的ひずみ波形で行った。

20 【0048】試験片の加熱には高周波加熱装置を用い、冷却は管内面に前記エア供給口から空気を吹き込むことにより行った。試験温度は200~800℃とし、拘束条件は50%拘束とした。

【0049】

【表1】

| | | (wt%) | | | | | | | | | | | | | | | | | (v1%) | |
|------------------|----|-------|------|------|-------|-------|------|------|------|------|-------|-------|-----|-----|------|--------|-------|------|-------|--|
| 供試材 | | C | Si | Mn | P | S | Cr | Ni | Nb | Ti | Al | N | Mo | W | V | B | (C+N) | A | 2×N | |
| 本 発 明 鋼 | 1 | 0.008 | 0.25 | 0.45 | 0.021 | 0.001 | 12.0 | 0.12 | 0.34 | 0.10 | 0.001 | 0.009 | - | - | - | - | 0.017 | 25.9 | 0.018 | |
| | 2 | 0.008 | 0.35 | 0.40 | 0.019 | 0.002 | 11.5 | 0.11 | 0.32 | 0.08 | 0.001 | 0.006 | - | - | - | - | 0.014 | 28.6 | 0.012 | |
| | 3 | 0.007 | 0.28 | 0.31 | 0.018 | 0.001 | 12.8 | 0.08 | 0.25 | 0.15 | 0.001 | 0.008 | - | - | - | - | 0.015 | 26.7 | 0.018 | |
| | 4 | 0.006 | 0.24 | 0.56 | 0.015 | 0.001 | 13.8 | 0.20 | 0.28 | 0.12 | 0.001 | 0.005 | - | - | - | - | 0.011 | 36.4 | 0.010 | |
| | 5 | 0.006 | 0.36 | 0.42 | 0.018 | 0.002 | 11.8 | 0.26 | 0.31 | 0.10 | 0.002 | 0.006 | - | - | - | - | 0.012 | 34.2 | 0.012 | |
| | 6 | 0.009 | 0.29 | 0.44 | 0.025 | 0.001 | 12.1 | 0.12 | 0.33 | 0.08 | 0.025 | 0.008 | - | - | - | - | 0.017 | 24.1 | 0.018 | |
| | 7 | 0.008 | 0.28 | 0.34 | 0.015 | 0.001 | 11.9 | 0.09 | 0.35 | 0.08 | 0.042 | 0.007 | - | - | - | - | 0.015 | 28.7 | 0.017 | |
| | 8 | 0.007 | 0.26 | 0.45 | 0.019 | 0.001 | 12.2 | 0.16 | 0.36 | 0.09 | 0.081 | 0.008 | - | - | - | - | 0.015 | 30.0 | 0.016 | |
| | 9 | 0.009 | 0.38 | 0.33 | 0.018 | 0.001 | 11.7 | 0.07 | 0.32 | 0.10 | 0.021 | 0.006 | 1.2 | - | - | - | 0.015 | 28.0 | 0.012 | |
| | 10 | 0.009 | 0.26 | 0.42 | 0.021 | 0.001 | 11.9 | 0.21 | 0.33 | 0.10 | 0.001 | 0.008 | - | 0.5 | - | - | 0.017 | 25.3 | 0.016 | |
| | 11 | 0.007 | 0.22 | 0.36 | 0.019 | 0.002 | 12.5 | 0.17 | 0.41 | 0.06 | 0.001 | 0.009 | - | - | 0.25 | - | 0.016 | 29.4 | 0.018 | |
| | 12 | 0.010 | 0.20 | 0.55 | 0.015 | 0.002 | 13.0 | 0.18 | 0.32 | 0.10 | 0.001 | 0.006 | - | - | - | 0.0005 | 0.016 | 26.2 | 0.012 | |
| | 13 | 0.008 | 0.28 | 0.32 | 0.025 | 0.001 | 12.2 | 0.15 | 0.36 | 0.07 | 0.001 | 0.009 | 0.8 | - | - | 0.0007 | 0.017 | 25.3 | 0.018 | |
| | 14 | 0.011 | 0.22 | 0.41 | 0.028 | 0.001 | 11.6 | 0.08 | 0.50 | 0.06 | 0.001 | 0.006 | - | - | - | - | 0.017 | 32.9 | 0.012 | |
| | 15 | 0.007 | 0.25 | 0.38 | 0.021 | 0.001 | 12.4 | 0.12 | 0.21 | 0.20 | 0.001 | 0.006 | - | - | - | - | 0.013 | 31.5 | 0.012 | |
| | 16 | 0.008 | 0.21 | 0.35 | 0.020 | 0.001 | 11.2 | 0.06 | 0.29 | 0.08 | 0.024 | 0.005 | 0.4 | 0.8 | - | - | 0.013 | 28.5 | 0.010 | |
| | 17 | 0.007 | 0.23 | 0.42 | 0.019 | 0.001 | 11.4 | 0.08 | 0.28 | 0.10 | 0.028 | 0.006 | 0.6 | - | 0.22 | 0.0003 | 0.013 | 29.2 | 0.012 | |
| | 18 | 0.009 | 0.24 | 0.37 | 0.021 | 0.001 | 11.3 | 0.10 | 0.25 | 0.08 | 0.001 | 0.007 | 0.3 | 0.6 | 0.20 | 0.0003 | 0.016 | 20.6 | 0.014 | |
| 比 較 鋼 | 19 | 0.010 | 0.44 | 0.31 | 0.022 | 0.002 | 11.3 | 0.09 | 0.01 | 0.25 | 0.001 | 0.009 | - | - | - | - | 0.019 | 13.7 | 0.018 | |
| | 20 | 0.010 | 1.30 | 0.30 | 0.022 | 0.002 | 11.3 | 0.20 | 0.20 | 0.25 | 0.050 | 0.015 | - | - | - | - | 0.025 | 18.0 | 0.030 | |
| | 21 | 0.015 | 1.64 | 0.44 | 0.020 | 0.002 | 12.2 | 0.06 | 0.38 | 0.17 | 0.001 | 0.012 | - | - | - | - | 0.027 | 20.4 | 0.024 | |
| | 22 | 0.012 | 0.02 | 0.32 | 0.022 | 0.001 | 11.5 | 0.12 | 0.45 | 0.15 | 0.001 | 0.011 | - | - | - | - | 0.023 | 26.1 | 0.022 | |
| | 23 | 0.009 | 0.43 | 0.44 | 0.021 | 0.002 | 11.8 | 0.23 | 0.75 | 0.15 | 0.001 | 0.008 | - | - | - | - | 0.017 | 52.9 | 0.016 | |
| | 24 | 0.011 | 0.55 | 0.43 | 0.018 | 0.002 | 12.2 | 0.19 | 0.20 | 0.05 | 0.001 | 0.013 | - | - | - | - | 0.024 | 10.4 | 0.026 | |
| | 25 | 0.008 | 0.35 | 0.28 | 0.019 | 0.001 | 11.8 | 0.11 | 0.34 | 0.16 | 0.002 | 0.010 | 2.8 | - | - | - | 0.018 | 27.8 | 0.020 | |
| | 26 | 0.015 | 0.36 | 0.38 | 0.020 | 0.001 | 12.4 | 0.08 | 0.45 | 0.10 | 0.001 | 0.010 | - | - | - | - | 0.025 | 22.0 | 0.020 | |
| | 27 | 0.010 | 0.35 | 0.33 | 0.024 | 0.001 | 13.2 | 0.10 | 0.29 | 0.10 | 0.022 | 0.010 | - | - | - | - | 0.020 | 19.5 | 0.020 | |

比較鋼19はSUH509L相当鋼

A: (Nb+Ti)/(C+H)

□: 本発明の規定範囲外を示す

【0050】熱延板を600℃で1000時間時効し、4mm厚さのJIS4号シャルピー試験片をT方向に採取して靱性を評価した。また、熱延板に開先加工を施し表※50

※2に示す条件で突き合わせTIG溶接を行ない、溶接熱影響部にノッチがくるように4mm厚さのJIS4号シャルピー試験片を採取した。

【0051】

【表2】

(表2)

| | |
|------|-------------|
| フィラー | 410Nb、直径2mm |
| 溶接電流 | 90~100A |
| 溶接電圧 | 13V |
| 溶接速度 | 10cm/min |

【0052】熱延焼鈍材と熱延焼鈍材を600℃で1000時間時効した材料から3mm厚の板状引張試験片を採取し、600℃で試験を行った。

【0053】酸化試験は、800℃で200時間、大気中連続加熱条件で行った。

【0054】上記各種の試験結果を表3、4に示す。表4は熱延板を焼鈍した後時効した材料の試験結果を示す。

*す。同表より、本発明鋼1~18は、常温伸び30%以上、600℃の引張り強度25N/mm²以上、800℃における酸化増量が2.0mg/cm²以下、熱疲労寿命2000サイクル以上と、加工性、高温強度、耐酸化性、熱疲労強度に優れることがわかる。また、本発明鋼は溶接熱影響部のvTrEは0℃以下で、時効後の常温塑性も使用上問題とならないレベルであることが確認された。

【0055】特に、本発明鋼6~8に示すように0.02~0.2%のAlを添加すると、溶接熱影響部の塑性が向上することが確認された。また、本発明鋼9、13、16、18で特に、Mo、W添加によって熱疲労強度が向上し、時効後の強度低下が低減されることが確認された。

【0056】

【表3】

(表3)

| 供試鋼 | | 冷間圧延材料 | | | 熱間圧延材料 | |
|------|----|---------|---------------------------|---------------|--------------------------------|---------------|
| | | 常温伸び(X) | 酸化増量(mg/cm ²) | 熱疲労寿命(cycles) | 600℃の引張り強度(N/mm ²) | 溶接熱影響部vTrE(℃) |
| 本発明鋼 | 1 | 35 | 1.5 | 2250 | 30 | -15 |
| | 2 | 33 | 1.2 | 2300 | 31 | -10 |
| | 3 | 34 | 1.1 | 2120 | 27 | -12 |
| | 4 | 37 | 1.4 | 2200 | 29 | -18 |
| | 5 | 38 | 1.3 | 2190 | 28 | -16 |
| | 6 | 38 | 1.2 | 2150 | 29 | -18 |
| | 7 | 35 | 1.0 | 2180 | 29 | -20 |
| | 8 | 38 | 1.0 | 2340 | 31 | -22 |
| | 9 | 35 | 1.2 | 2290 | 32 | -5 |
| | 10 | 36 | 1.4 | 2190 | 29 | -8 |
| | 11 | 38 | 1.8 | 2390 | 32 | -11 |
| | 12 | 36 | 1.5 | 2180 | 29 | -10 |
| | 13 | 36 | 1.3 | 2320 | 31 | -7 |
| | 14 | 31 | 1.6 | 2300 | 31 | -1 |
| | 15 | 36 | 1.5 | 2100 | 26 | -15 |
| | 16 | 32 | 1.3 | 2450 | 31 | -8 |
| | 17 | 34 | 1.5 | 2400 | 31 | -5 |
| | 18 | 33 | 1.6 | 2480 | 32 | -7 |
| 比較鋼 | 19 | 37 | 1.4 | 1430 | 20 | -5 |
| | 20 | 29 | 0.7 | 1820 | 22 | 12 |
| | 21 | 26 | 0.8 | 2230 | 30 | 25 |
| | 22 | 34 | 3.5 | 2280 | 31 | -2 |
| | 23 | 25 | 1.1 | 2130 | 35 | 28 |
| | 24 | 36 | 1.2 | 1800 | 22 | -18 |
| | 25 | 27 | 1.0 | 2470 | 34 | 0 |
| | 26 | 32 | 1.2 | 2060 | 26 | 20 |
| | 27 | 35 | 1.4 | 2150 | 30 | 10 |

【0057】

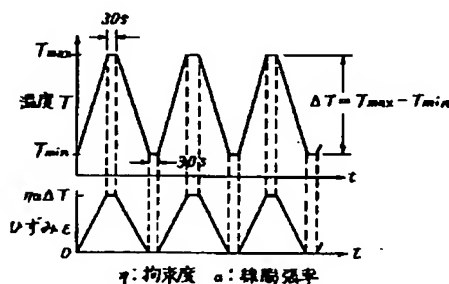
【表4】

10

20

【図2】熱疲労試験時の温度及びひずみ波形を示す図である。

【図2】



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CLAIMS

[Claim(s)]

[Claim 1] By weight %, below C:0.015 % and under Si:0.2 - 0.8 % Mn: Below [under 0.2 - 0.8 %, / P:0.03% or less and below S:0.002 %], Nb:0.2 % is exceeded below nickel:0.5 % Cr:11-14%. Below 0.5 % Ti: 0.06-0.2 %, below N:0.015 %, aluminum:0 - 0.2 %, It is the heat-resistant ferritic stainless steel with which $\text{aluminum} \geq 2N$ is satisfied when it contains and $(\text{Nb} + \text{Ti}) / (\text{C} + \text{N}) \geq 20$ and aluminum are included $\text{C} + \text{N} \leq 0.02\%$, and the remainder consists of Fe and an unescapable impurity.

[Claim 2] Furthermore, heat-resistant ferritic stainless steel according to claim 1 characterized by one sort or including two or more sorts in below Mo:0.3 - 2 %, W:0.1 - 1 %, V:0.1 - 0.5 %, and B:0.0003 - 0.005 %

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to heat-resistant ferritic stainless steel suitable as various internal combustion engines' exhaust gas path member. For example, it is suitable for an automobile exhaust air system member and the exhaust gas path member of LNG thermal power combined cycle power generation using an exhaust-heat-recovery boiler.

[0002]

[Description of the Prior Art] Exhaust air system components, such as an automobile exhaust manifold, a front pipe, and a pin center, large pipe (henceforth automobile exhaust air system tubing), are in the part in contact with the hot combustion gas discharged from an engine, and various properties, such as outstanding workability, and oxidation resistance, high temperature strength, a heat-resistant fatigability, are required of the ingredient which constitutes this. However, in order to respond to the rise of strengthening of emission control in recent years, and the exhaust gas temperature according to improvement in the engine performance of an automobile further, the request of the improvement in fuel consumption by car-body metrization, etc., the welded tube of stainless steel has come to be used as an exhaust air system ingredient.

[0003] on the other hand -- a thermal power station plant -- if it is, the combined cycle power generation using an exhaust-heat-recovery boiler is performed briskly, and the combustion temperature of the turbine for a generation of electrical energy tends to rise, and from using especially LNG as a fuel, from the conventional 1100-degree-C class, 1300-degree-C class and 1350-degree-C class make a plan, and are actually coming to install it in recent years. In connection with it, the exhaust-heat-recovery boiler which collects the heat of the elevated-temperature exhaust gas by the side of turbine appearance is also in the elevated-temperature-ized inclination. For example, conventionally, the exhaust gas temperature which it was around 550 degrees C rises by about 100 degrees C, and is becoming before and after 650 degrees C.

[0004] Austenitic stainless steel has the outstanding thermal resistance and workability, and weldability. As a typical steel type, there are SUS304 (18Cr-8nickel), SUS310S (25Cr-20 nickel), etc. However, the coefficient of thermal expansion of austenitic stainless steel is large, and destruction tends to produce it by the thermal fatigue resulting from heat distortion in the application which receives the repeat of intense heating-cooling like an automobile exhaust pipe.

[0005] Moreover, generally the exhaust-heat-recovery boiler of LNG thermal power combined cycle power generation takes the operation method of a day-ranges operation-Nighttime halt except for a power consumption peak term, such as midsummer. Therefore, in an exhaust heat path member, when an austenitic stainless steel is used for example, for a lining duct etc., since the coefficient of thermal expansion is large, there is risk, such as deformation by heat distortion.

[0006] On the other hand, since the coefficient of thermal expansion is smaller than austenitic stainless steel, since it is cheap, when ferritic stainless steel can avoid fatigue breaking and deformation by such heat distortion, and the direction of ferritic stainless steel uses for an automobile exhaust pipe, a lining

duct, etc., it becomes advantageous.

[0007] the thermal resistance in 600 degrees C or more -- especially -- the field of creep strength -- ferritic stainless steel -- an austenitic stainless steel -- it should also reach -- although there is nothing, taking advantage of that a coefficient of thermal expansion is small and the advantage of being cheap, it can be said that it is suitable for the structural member as which creep strength is not required so much as mentioned above. Conventionally, generally as heat-resistant ferritic stainless steel, SUH409L (12 Cr-Ti) has been used. However, an ingredient which was further excellent in high temperature strength and creep strength was desired with the rise of the exhaust gas temperature of an automobile exhaust air system and an exhaust-heat-recovery boiler.

[0008] Furthermore, in the exhaust gas of the exhaust-heat-recovery boiler of LNG thermal power combined cycle power generation, about 10% of moisture and about 5% of carbon dioxide gas are contained, we are anxious about the dew point corrosion at the time of the shutdown by these water of condensation, and especially a corrosion-resistant improvement by the weld zone was desired.

[0009] "JP,60-145359,A C:0.05% or less, Si:1.0 - 2.0 %, Mn: Below 2 %, Cr:6 -25%, less than [Mo:5%] (However, Cr+Mo>=8 %), N:0.05% or less, and below aluminum:0.5 % one or more (however, Ti, Zr, Ta, and the amount of Nb(s) -- all C --) sorts of Ti, Zr, Ta, and Nb The amount of stoichiometries required to use N as carbide and a nitride is included, and it is Nb. : The high-temperature-service ferritic steel which moreover consists of un-joining [Nb] together more than 0.1 % (preferably more than 0.2 %) (dissolution) at 0.3% or less and which has periodic oxidation resistance and creep strength" is indicated.

[0010] In this official report, addition of Si is effective in periodic oxidation resistance, and it is said to creep strength that formation of the Laves phase which is rich in the existence of un-joining [Nb] together (dissolution) and Si more than 0.1 % (preferably more than 0.2 %) is important.

[0011] However, when 1% or more of Si is made to contain as a result of this invention persons' examining the above-mentioned ferritic steel, acquiring good base material toughness stiffens by the Laves phase which deposits during elevated-temperature use rather than it is easy, and it has risk of breaking with a small impact at the time of a temperature fall. When a thick plate was used as a structural member while calling it especially 3-9mm of board thickness, it became clear that the dependability at the time of long duration use is not acquired. Moreover, there is a problem that the steel currently indicated by the example of this invention has few Nb(s) and the amounts of Ti which contribute to stabilization of C and N, and is inadequate for preventing the intergranular corrosion of a heat affected zone.

[0012] In JP,62-14626,B, it is the inside S and O of steel. It considers as less than 0.008%, and the ferritic steel the inclusion in steel excelled [ferritic steel] in the elevated temperature at the high-temperature-oxidation-proof nature characterized by being inclusion more stable than MnS is indicated.

[0013] MnS or Cr which is the inclusion which has a bad influence on oxidation resistance by reducing the content of S and O which are an impurity, In order to be characterized by suppressing generation of oxysulfides, such as Si, aluminum, and Mn, and to control oxidation-resistant degradation by the time of elevated-temperature use, or Cr carbide generation of a weld zone Adding one sort of Ti, Nb, Zr, and Ta or two sorts or more in total as a C fixed element in 4 or more times of the amount of C and 1.5% or less of range is indicated.

[0014] However, the examination about N of an impurity is not made, and since the effect of N affect the toughness of a base material and a weld zone is large, anxiety remains in the toughness of a weld zone especially. Moreover, the examination about the effect of many elements exerted on high temperature strength and a thermal fatigue life is not made enough.

[0015] When two sorts of Ti, Nb(s), Ta, and Zr which are C and N fixed element are added especially, the examination about the workability at the time of carrying out compound addition of Nb and Ti, a moldability, toughness, high temperature strength, and the proper addition that considered corrosion resistance balance is not made.

[0016]

[Problem(s) to be Solved by the Invention] Especially this invention has high temperature strength and a

heat-resistant fatigability excellent in the exhaust gas temperature of 600-650 degrees C compared with the conventional steel of SUH409 grade, and aims at obtaining the ferritic stainless steel which was suitable as an automobile exhaust air system member with the oxidation resistance to 800 degrees C, the outstanding workability and weld zone corrosion resistance, and toughness, or an exhaust gas path member of LNG thermal power combined cycle power generation. Moreover, it is in offer of the ingredient contributed to unification of the cheap ferritic-stainless-steel material which can respond also to a user's low cost-ization, for example, the ingredient which results in an exhaust manifold-front pin center, large pipe-muffler in an automobile exhaust air system.

[0017]

[Means for Solving the Problem] Generally, it is the sheet metal or the welded tube of 2mm or less of board thickness, and as board thickness of exhaust-heat-recovery boiler duct material, 1.5-6mm is a subject and, as for an automobile exhaust air system member, the inside thick plate to about 9mm is also used. Required oxidation resistance, high temperature strength, a heat-resistant fatigue property, workability, toughness, and weldability are required for all on structure. However, what is necessary is not to require the creep strength of SUS304 or the 2.25Cr(s)-1Mo ferritic steel average, since it is the member which does not receive severe internal pressure etc., but just to provide the high temperature strength which can be equal to long-term use.

[0018] Then, that the ferritic steel in which many above-mentioned properties were more excellent compared with steel conventionally should be developed, this invention persons came to acquire the following knowledge, as a result of inquiring wholeheartedly.

[0019] A) -- Nb the pole of 0.006 - 0.2 % -- the carbide formed when the compound addition effectiveness of Ti of the narrow range is carried out (Nb, Ti) Since the field (Interstitial Free) where Dissolution C and N does not exist around it since it is easy to deposit as a nucleus is formed, TiN which deposits at an elevated temperature and deposits minutely rather than the carbide in Nb or Ti independent addition system Although this becomes elasticity and good workability and a moldability are obtained Since the sites a Laves phase carries out [sites] a priority deposit decrease in number to coincidence, it is effective in deposit delay of a Laves phase elevated-temperature in use, embrittlement can be delayed and recrystallizing temperature is also reduced further, ease heat distortion and a thermal fatigue property should improve.

[0020] B) -- while the toughness of a base material and a heat affected zone improves by regulating with $(Nb+Ti)/(C+N) \geq 20$, the intergranular corrosion of the weld zone in a water-of-condensation environment should be prevented.

[0021] C) -- the toughness of the amount of aluminum added in order to raise oxidation resistance and toughness in a hot-rolling plate and a heat affected zone should improve by being referred to as $aluminum \geq 2N$ 0.02% or more.

[0022] This invention is what was completed based on such knowledge. The summary "At % of the weight, below C:0.015 % and under Si:0.2 - 0.8 % Mn: Less than [0.2 -0.8%], P:0.03% or less, and below S:0.002 % Nb:0.2 % is exceeded below nickel:0.5 % Cr:11-14%. According to aluminum:0 - 0.2 % and the need below 0.5 % and Ti:0.06-0.2 % and below N:0.015 % Mo: 0.3 - 2 %, W:0.1 - 1 %, V:0.1 - 0.5 %, In below B:0.0003 - 0.005 %, one sort or when two or more sorts are included and $(Nb+Ti)/(C+N) \geq 20$ and aluminum are included $C+N \leq 0.02\%$, $aluminum \geq 2N$ is satisfied, and it is in the heat-resistant ferritic stainless steel with which the remainder consists of Fe and an unescapable impurity."

[0023]

[Function] Next, a content and an operation are explained about the alloy content and impurity of this invention steel.

[0024] Although reinforcement is raised, toughness is degraded, and the increment in C and N:C, and N is ***** about a bad influence to workability and weldability. Therefore, the thing low as much as possible of C and N is desirable, and, for this reason, they carry out to below C:0.015 % and below N:0.015 %, and may be $C+N \leq 0.02\%$. They are below N:0.010 % and below $C+N:0.015\%$ C:0.01% or less desirably.

[0025] If C+N exceeds 0.03%, even if it will carry out compound addition of Ti and the Nb, while C and

N cannot be fixed enough and said bad influence comes out, the intergranular corrosion susceptibility of a weld zone becomes high.

[0026] Si:Si is an effective deoxidation element and is an element indispensable to oxidation resistance. 0.2 Demonstrate effectiveness on an anti-oxidation disposition by the addition more than %. Moreover, there is effectiveness of raising high temperature strength and raising a heat-resistant fatigue property in Si. In the Laves phase (mainly Fe₂Nb) which deposits at an elevated temperature (> 600 degrees C), this is for suppressing the fall of the dissolution Nb which contributes to high temperature strength, and holding high temperature strength, when Si permutes a part of Nb. 0.8 If it adds more than %, since toughness and workability will be degraded, Si needs to be taken as the narrow range under 0.2 - 0.8 %. It is 0.2 - 0.6 % desirably.

[0027] Mn:Mn is a deoxidation element and is known as an element which improves hot-working nature. However, MnS is formed, and since the origin of oxidation comes or it is an austenite formation element, it is not desirable for oxidation resistance. Therefore, it carried out to under 0.2 - 0.8 %. It is 0.3 - 0.7 % desirably.

[0028] Cr: It is an element indispensable to oxidation resistance and corrosion resistance. At less than 11%, if the effectiveness does not show up but it adds exceeding 14%, in order to degrade toughness and workability, the upper limit was made into 14%.

[0029] P: Although P is one of the unescapable impurities on manufacture, in order to avoid the bad influence to toughness and workability, it is 0.03% or less.

[0030] S: If there are many amounts of S, like Mn, it is not desirable from an oxidation-resistant point, and since it has a bad influence also on weldability, it is necessary to make an upper limit into 0.002 %, although S is also an unescapable impurity on manufacture.

[0031] Nb:Nb is an element indispensable when raising the high temperature strength and creep strength which are the weak spot of ferritic stainless steel, and the effectiveness shows up notably above 500 degrees C. Nb has the operation which fixes C and N as carbon nitride. In this invention, Nb:0.2 % is exceeded, and below 0.5 %, since it is considering as $C+N \leq 0.02\%$, it is set to $\%Nb/(\%C+\%N) \geq 10$. The amount of dissolution Nb(s) required for this to obtain sufficient high temperature strength and creep strength was secured. Since the deposit of a Laves phase became remarkable and toughness deteriorated when high temperature strength sufficient by below 0.2 % was not obtained from the point of high temperature strength although it was so desirable that many, but contained exceeding 0.5 %, the amount of Nb(s) exceeded 0.2 %, and made it below 0.5 %.

[0032] Although the Laves phase (Fe₂Nb) deposited during elevated-temperature use (>600 **) and the fall of the high temperature strength by the fall of the amount of dissolution Nb(s) took place, it found out that it was required more than 0.1 % as an amount of dissolution Nb(s) to obtain high temperature strength sufficient also after a deposit, therefore the amount of Nb(s)-beyond 0.3 % was required. Moreover, since the total amount of Laves phase deposits decreases as much as possible from the point of embrittlement by Laves phase deposit so that the amount of Nb(s) is low, a desirable upper limit is 0.4 %.

[0033] Ti:Ti is effective as a fixed element of C and N like Nb. In a heat affected zone, generation of Cr carbide is controlled especially, and they are toughness and an element indispensable to corrosion resistance reservation. Moreover, in Ti and Nb, it has a base material and the coarsening depressor effect of a heat affected zone. In order to fully demonstrate such effectiveness, it needs $(Nb+Ti)/(C+N) \geq 20$. desirably, such effectiveness is demonstrated further -- making -- (Ti/Nb) -- about 0.5 -- general -- 0.2 the above -- 1.0 It is good to consider as the following.

[0034] When Nb and Ti carry out compound addition, Ti combines with N and forms a nitride, and Nb and remaining Ti combine with C and mainly form carbide (Nb, Ti). As described above (Nb, Ti), carbide tends to deposit considering TiN which deposits at an elevated temperature rather than the carbide in Nb or Ti independent addition system, and deposits minutely as a nucleus. Therefore, the field (Interstitial Free) where Dissolution C and N does not exist is formed around it.

[0035] Although this becomes elasticity and good workability and a moldability are obtained, the sites a Laves phase carries out [sites] a priority deposit decrease in number to coincidence, it is effective in

deposit delay of a Laves phase elevated-temperature in use, and embrittlement can be delayed. Furthermore, since recrystallizing temperature is also reduced, heat distortion is eased and a thermal fatigue property improves.

[0036] From the purpose which demonstrates the above effectiveness, 0.06% or more of content is required for Ti, and 4 or more times of N are secured, and it is the minimum of the amount in which some carbide formation is possible. Since raising the above-mentioned effectiveness did not almost have the addition exceeding 0.2% and the surface crack at the time of rolling became remarkable, the upper limit was made into 0.2 %.

[0037] nickel:nickel is one of the unescapable impurities on manufacture. Although addition of nickel of a minute amount was effective in the toughness improvement, it carried out to below 0.5 % especially from the thing for which it has a bad influence on oxidation resistance.

[0038] aluminum:aluminum is an arbitration alloying element, and if it is known as a deoxidation element and coexists with Ti, it will become more remarkable [the effectiveness]. Moreover, it is known that toughness will improve by little aluminum addition. The toughness of a hot-rolling plate and a heat affected zone improves by being especially referred to as 2%N<=%aluminum. It is for acting on immobilization of N with Ti at the time of welding, and the initial complement is 2%N<=%aluminum.

[0039] Moreover, oxidation resistance improves by 0.02% or more of aluminum content. The peeling resistance of the scale is raised because aluminum carries out internal oxidation and carries out the role of a "wedge" to a scale especially, and oxidation resistance improves. Thereby, mixing of the scale to the inside of exhaust gas is controlled. Furthermore, 0.02% or more of aluminum also has high temperature strength and a creep strength improvement effect. However, superfluous addition made the upper limit 0.2 % in order to saturate the effectiveness to oxidation resistance and high temperature strength and to do a bad influence to workability.

[0040] Mo:Mo is an arbitration alloying element and is known like Nb as an element which raises high temperature strength. In order that unlike Nb the Laves phase (Fe₂ Mo) formation inclination of Mo may be smaller than Fe₂ Nb and it may hold a dissolution condition over a long period of time during elevated-temperature use, a solid-solution-strengthening operation is maintained. Therefore, to an improvement, Mo addition is desirable in creep strength and corrosion resistance. In this case, since below 0.3 % was not enough as those effectiveness, the minimum was made into 0.3 %. However, superfluous addition reduces toughness and workability. Since it furthermore became cost quantity, the upper limit was made into 2.0 % when adding.

[0041] W: W is an arbitration alloying element and is known as an element which raises high temperature strength like Nb and Mo. The formation inclination of W of a Laves phase is still smaller than Mo, and since a solid-solution-strengthening operation is maintained over a long period of time from **, creep strength improves. 0.1% or less was not enough as the effectiveness, and toughness and workability were degraded, and since superfluous addition served as cost quantity, it could be 0.1 - 1%.

[0042] V:V is an arbitration alloying element, and it improves workability while forming a dissolution condition or carbon nitride and raising high temperature strength. 0.1 The effectiveness shows up above %. However, since workability was reduced on the contrary when it was made to contain exceeding 0.5 %, it considered as 0.1 - 0.5 %.

[0043] B: B is an arbitration alloying element and make it contain in order to improve high temperature strength and oxidation resistance.

[0044] Although the reason the improvement effect shows up is not certain, since B is known as an element which is generally easy to segregate to a grain boundary, it is thought that a grain boundary skid is prevented and high temperature strength is improved. Moreover, it is thought that impurity elements, such as P harmful to oxidation resistance and S, are discharged, and oxidation resistance is raised by grain boundary segregation. This effectiveness showed up at 0.0003% or more, and since toughness and workability were also degraded when it was made to contain exceeding 0.005 %, it was made into 0.0003-0.005 %.

[0045]

[Example] First, it hot-rolled at 1150 degrees C whenever [stoving temperature] after the dissolution

and forging, the steel which has the presentation shown in Table 1 was annealed at finishing and 960 degrees C to 4.5mm of board thickness, and the hot-rolling plate was produced. Furthermore, it cold-rolled to the hot-rolling plate of 4.5mm thickness, finishing annealing was performed at 960 degrees C, and the cold-rolled plate of 1.5mm of board thickness was produced. From cold rolled sheet steel, the piece of an oxidation test with an ordinary temperature test piece for tensile test with a thickness [1.5mm] of T to JIS13B No. and the thickness of 1.5mm, a width of face [of 20mm], and a die length of 25mm was extracted. The cold-rolled plate was manufactured with electric resistance welding, and the thermal fatigue test piece was produced.

[0046] Drawing 1 is drawing showing the configuration of a thermal fatigue test piece, and is 1. It is tubing of a test coupon and is a path to two places. A 8mm hole (2 3) is broken and it is the feed hopper 3 of Ayr for cooling. It has become. 4 The holder (rodding) from the inside of ****, and 5 It is the installation section to the electrode holder of a testing machine. Tubing 1 Holder 4 Pin 6 for immobilization Weld zone 7 of an edge It is fixed.

[0047] The trial was performed in the thermal fatigue test using the electric hydraulic-servo type elevated-temperature thermal fatigue testing device of computer control under the temperature cycle shown in drawing 2, and the mechanical strain wave.

[0048] Cooling was carried out to heating of a test piece using high-frequency-heating equipment by blowing air into a tubing inside from said Ayr feed hopper. The test temperature was made into 200 - 800 **, and the constraint was considered as constraint 50%.

[0049]

[Table 1]

| | | (表 1) | | | | | | | | | | | | | | | | (wt%) | |
|------------------|----|-------|------|------|-------|-------|------|------|------|------|-------|-------|-----|-----|------|--------|-------|-------|-------|
| 供試鋼 | | C | Si | Mn | P | S | Cr | Ni | Nb | Ti | Al | N | Mo | W | V | B | (C+N) | A | 2×N |
| 本 発 明 鋼 | 1 | 0.008 | 0.25 | 0.45 | 0.021 | 0.001 | 12.0 | 0.12 | 0.34 | 0.10 | 0.001 | 0.009 | - | - | - | - | 0.017 | 25.9 | 0.018 |
| | 2 | 0.008 | 0.35 | 0.40 | 0.019 | 0.002 | 11.5 | 0.11 | 0.32 | 0.08 | 0.001 | 0.008 | - | - | - | - | 0.014 | 28.8 | 0.012 |
| | 3 | 0.007 | 0.28 | 0.31 | 0.018 | 0.001 | 12.8 | 0.08 | 0.25 | 0.15 | 0.001 | 0.008 | - | - | - | - | 0.015 | 26.7 | 0.016 |
| | 4 | 0.006 | 0.24 | 0.56 | 0.015 | 0.001 | 13.8 | 0.20 | 0.28 | 0.12 | 0.001 | 0.005 | - | - | - | - | 0.011 | 36.4 | 0.010 |
| | 5 | 0.006 | 0.36 | 0.42 | 0.018 | 0.002 | 11.8 | 0.26 | 0.31 | 0.10 | 0.002 | 0.006 | - | - | - | - | 0.012 | 34.2 | 0.012 |
| | 6 | 0.009 | 0.29 | 0.44 | 0.025 | 0.001 | 12.1 | 0.12 | 0.33 | 0.08 | 0.025 | 0.008 | - | - | - | - | 0.017 | 24.1 | 0.016 |
| | 7 | 0.008 | 0.28 | 0.34 | 0.015 | 0.001 | 11.9 | 0.09 | 0.35 | 0.08 | 0.042 | 0.007 | - | - | - | - | 0.015 | 28.7 | 0.017 |
| | 8 | 0.007 | 0.26 | 0.45 | 0.019 | 0.001 | 12.2 | 0.16 | 0.36 | 0.09 | 0.081 | 0.008 | - | - | - | - | 0.015 | 30.0 | 0.016 |
| | 9 | 0.009 | 0.36 | 0.33 | 0.018 | 0.001 | 11.7 | 0.07 | 0.32 | 0.10 | 0.021 | 0.006 | 1.2 | - | - | - | 0.015 | 28.0 | 0.012 |
| | 10 | 0.009 | 0.26 | 0.42 | 0.021 | 0.001 | 11.9 | 0.21 | 0.33 | 0.10 | 0.001 | 0.008 | - | 0.5 | - | - | 0.017 | 25.3 | 0.016 |
| | 11 | 0.007 | 0.22 | 0.36 | 0.019 | 0.002 | 12.5 | 0.17 | 0.41 | 0.06 | 0.001 | 0.009 | - | - | 0.25 | - | 0.016 | 29.4 | 0.018 |
| | 12 | 0.010 | 0.20 | 0.55 | 0.015 | 0.002 | 13.0 | 0.18 | 0.32 | 0.10 | 0.001 | 0.008 | - | - | - | 0.0005 | 0.016 | 26.2 | 0.012 |
| | 13 | 0.008 | 0.28 | 0.32 | 0.025 | 0.001 | 12.2 | 0.15 | 0.36 | 0.07 | 0.001 | 0.009 | 0.8 | - | - | 0.0007 | 0.017 | 25.3 | 0.018 |
| | 14 | 0.011 | 0.22 | 0.41 | 0.028 | 0.001 | 11.6 | 0.08 | 0.50 | 0.06 | 0.001 | 0.006 | - | - | - | - | 0.017 | 32.9 | 0.012 |
| | 15 | 0.007 | 0.25 | 0.36 | 0.021 | 0.001 | 12.4 | 0.12 | 0.21 | 0.20 | 0.001 | 0.008 | - | - | - | - | 0.013 | 31.5 | 0.012 |
| | 16 | 0.008 | 0.21 | 0.35 | 0.020 | 0.001 | 11.2 | 0.06 | 0.29 | 0.08 | 0.024 | 0.005 | 0.4 | 0.8 | - | - | 0.013 | 28.5 | 0.010 |
| | 17 | 0.007 | 0.23 | 0.42 | 0.019 | 0.001 | 11.4 | 0.08 | 0.28 | 0.10 | 0.028 | 0.008 | 0.6 | - | 0.22 | 0.0003 | 0.013 | 29.2 | 0.012 |
| | 18 | 0.009 | 0.24 | 0.37 | 0.021 | 0.001 | 11.3 | 0.10 | 0.25 | 0.08 | 0.001 | 0.007 | 0.3 | 0.6 | 0.20 | 0.0003 | 0.016 | 20.6 | 0.014 |
| 比 較 鋼 | 19 | 0.010 | 0.44 | 0.31 | 0.022 | 0.002 | 11.3 | 0.09 | 0.01 | 0.25 | 0.001 | 0.009 | - | - | - | - | 0.019 | 13.7 | 0.018 |
| | 20 | 0.010 | 1.30 | 0.30 | 0.022 | 0.002 | 11.3 | 0.20 | 0.20 | 0.25 | 0.050 | 0.015 | - | - | - | - | 0.025 | 18.0 | 0.030 |
| | 21 | 0.015 | 1.64 | 0.44 | 0.020 | 0.002 | 12.2 | 0.06 | 0.38 | 0.17 | 0.001 | 0.012 | - | - | - | - | 0.027 | 20.4 | 0.024 |
| | 22 | 0.012 | 0.02 | 0.32 | 0.022 | 0.001 | 11.5 | 0.12 | 0.45 | 0.15 | 0.001 | 0.011 | - | - | - | - | 0.023 | 26.1 | 0.022 |
| | 23 | 0.009 | 0.43 | 0.44 | 0.021 | 0.002 | 11.8 | 0.23 | 0.75 | 0.15 | 0.001 | 0.008 | - | - | - | - | 0.017 | 52.9 | 0.016 |
| | 24 | 0.011 | 0.55 | 0.43 | 0.018 | 0.002 | 12.2 | 0.19 | 0.20 | 0.05 | 0.001 | 0.013 | - | - | - | - | 0.024 | 10.4 | 0.026 |
| | 25 | 0.008 | 0.35 | 0.28 | 0.019 | 0.001 | 11.8 | 0.11 | 0.34 | 0.16 | 0.002 | 0.010 | 2.8 | - | - | - | 0.018 | 27.8 | 0.020 |
| | 26 | 0.015 | 0.36 | 0.38 | 0.020 | 0.001 | 12.4 | 0.08 | 0.45 | 0.10 | 0.001 | 0.010 | - | - | - | - | 0.025 | 22.0 | 0.020 |
| | 27 | 0.010 | 0.35 | 0.33 | 0.024 | 0.001 | 13.2 | 0.10 | 0.29 | 0.10 | 0.022 | 0.010 | - | - | - | - | 0.020 | 19.5 | 0.020 |

比較鋼19はSUH509L相当鋼

A : (Nb+Ti) / (C+N)

☐ : 本発明の規定範囲外を示す

[0050] Aging of the hot-rolling plate was carried out at 600 degrees C for 1000 hours, the piece of a JIS No. 4 Charpy test of 4mm thickness was extracted in the direction of T, and toughness was evaluated. Moreover, it compared on the conditions which perform edge preparation to a hot-rolling plate, and are shown in Table 2, and TIG arc welding was performed, and the piece of a JIS No. 4 Charpy test of 4mm thickness was extracted so that a notch might come to a heat affected zone.

[0051]

[Table 2]

(表 2)

| | |
|------|-------------|
| フィラー | 410Nb、直径2mm |
| 溶接電流 | 90~100A |
| 溶接電圧 | 13V |
| 溶接速度 | 10cm/min |

[0052] The tabular test piece for tensile test of 3mm thickness was extracted from the ingredient which carried out aging of a hot-rolling annealed material and the hot-rolling annealed material at 600 degrees C for 1000 hours, and it examined at 600 degrees C.

[0053] Continuation-among atmospheric air heating conditions performed the oxidation test at 800 degrees C for 200 hours.

[0054] Various kinds of above-mentioned test results are shown in Tables 3 and 4. Table 4 shows the test result of the ingredient which carried out aging, after annealing a hot-rolling plate. From this table, this invention steel 1-18 is 2 the ordinary temperature elongation of 30% or more, and the tensile strength of 25Ns/mm of 600 degrees C. It turns out above that the oxidation increase in quantity in 800 degrees C is excellent in two or less 2.0 mg/cm, 2000 or more cycles of thermal fatigue lives, workability, high temperature strength and oxidation resistance, and thermal fatigue reinforcement. Moreover, it was checked that this invention steel is level from which it is 0 degree C or less, and, as for vTrE of a heat affected zone, the ordinary temperature toughness after aging does not pose a use top problem, either.

[0055] As especially shown in this invention steel 6-8, when aluminum of 0.02 - 0.2 % was added, it was checked that the toughness of a heat affected zone improves. Moreover, it was checked that thermal fatigue reinforcement improves and the fall on the strength after aging is reduced by Mo and W addition especially with this invention steel 9, 13, 16, and 18.

[0056]

[Table 3]

(表 3)

| 供試鋼 | | 冷間圧延材料 | | | 熱間圧延材料 | |
|------------------|----|------------|-------------------------------|-------------------|-----------------------------------|-------------------|
| | | 常温 び(%) | 酸化増量 (mg/cm ²) | 熱疲労寿命 (cycles) | 600℃の引張 強度(N/mm ²) | 溶接熱影響部 vTrE(℃) |
| 本 発 明 鋼 | 1 | 35 | 1.5 | 2250 | 30 | -15 |
| | 2 | 33 | 1.2 | 2300 | 31 | -10 |
| | 3 | 34 | 1.1 | 2120 | 27 | -12 |
| | 4 | 37 | 1.4 | 2200 | 29 | -18 |
| | 5 | 36 | 1.3 | 2190 | 28 | -16 |
| | 6 | 36 | 1.2 | 2150 | 29 | -18 |
| | 7 | 35 | 1.0 | 2160 | 29 | -20 |
| | 8 | 36 | 1.0 | 2340 | 31 | -22 |
| | 9 | 35 | 1.2 | 2290 | 32 | -5 |
| | 10 | 36 | 1.4 | 2190 | 29 | -8 |
| | 11 | 36 | 1.8 | 2380 | 32 | -11 |
| | 12 | 36 | 1.5 | 2160 | 29 | -10 |
| | 13 | 36 | 1.3 | 2320 | 31 | -7 |
| | 14 | 31 | 1.6 | 2300 | 31 | -1 |
| | 15 | 36 | 1.5 | 2100 | 26 | -15 |
| | 16 | 32 | 1.3 | 2450 | 31 | -6 |
| | 17 | 34 | 1.5 | 2400 | 31 | -5 |
| | 18 | 33 | 1.6 | 2480 | 32 | -7 |
| 比 較 鋼 | 19 | 37 | 1.4 | 1430 | 20 | -5 |
| | 20 | 29 | 0.7 | 1820 | 22 | 12 |
| | 21 | 26 | 0.8 | 2230 | 30 | 25 |
| | 22 | 34 | 3.5 | 2280 | 31 | -2 |
| | 23 | 25 | 1.1 | 2130 | 35 | 28 |
| | 24 | 36 | 1.2 | 1800 | 22 | -18 |
| | 25 | 27 | 1.0 | 2470 | 34 | 0 |
| | 26 | 32 | 1.2 | 2060 | 26 | 20 |
| | 27 | 35 | 1.4 | 2150 | 30 | 10 |

[0057]

[Table 4]

(表 4)

| 供試鋼 | | 熱間圧延材料 | |
|------------------|----|---|------------------------------------|
| | | 25℃の衝撃値 vE ₀ (J/cm ²) | 600℃の引張り 強度(N/mm ²) |
| 本 発 明 鋼 | 1 | 56 | 20 |
| | 2 | 52 | 21 |
| | 3 | 58 | 18 |
| | 4 | 60 | 18 |
| | 5 | 55 | 17 |
| | 6 | 59 | 18 |
| | 7 | 62 | 18 |
| | 8 | 55 | 20 |
| | 9 | 52 | 23 |
| | 10 | 53 | 20 |
| | 11 | 58 | 21 |
| | 12 | 57 | 19 |
| | 13 | 55 | 22 |
| | 14 | 48 | 21 |
| | 15 | 56 | 18 |
| | 16 | 55 | 25 |
| | 17 | 58 | 25 |
| | 18 | 60 | 26 |
| 比 較 鋼 | 19 | 250 | 13 |
| | 20 | 12 | 13 |
| | 21 | 8 | 20 |
| | 22 | 71 | 18 |
| | 23 | 8 | 20 |
| | 24 | 73 | 13 |
| | 25 | 52 | 24 |
| | 26 | 10 | 18 |
| | 27 | 12 | 22 |

[0058] Although the comparison steel 19 is a SUH409L equivalent material, the tensile strength in 600 degrees C and a thermal fatigue property are inferior in it. Nb the comparison steel 20 and 24 Since it is 0.2% or less, the tensile strength in 600 degrees C and a thermal fatigue property are inferior. Since Mo of 0.8% or more and the comparison steel 25 was 2% or more and the comparison steel 21 was inferior to less than 30% of ordinary temperature elongation, and workability in Si, tube manufacturing of it was not completed easily. Since Si is less than 0.2%, the comparison steel 22 is inferior to oxidation resistance. Its amount of on-the-strength falls is also large while the comparison steel 23 is inferior to workability and the toughness of a heat affected zone and its embrittlement is [the impact resistance value after aging is low and] remarkable, since Nb is over 0.5%.

[0059] Since Si is 0.8% or less, the comparison steel 21 and 23 is zero or more, and vTrE is inferior to the ordinary temperature toughness after aging in it.

[0060] Since the comparison steel 26 and 27 is $C+N \geq 0.02$ and $(Nb+Ti)/(C+N) \leq 20$, respectively, it is inferior to the toughness of a heat affected zone.

[0061] In addition, it is checking that this invention steel of $(Nb+Ti)/(C+N) \geq 20$ does not generate intergranular corrosion by the Strauss test of the metal-active-gas-arc-welding section. However, when $(Nb+Ti)/(C+N)$ was less than 20 like the comparison steel 1 and 2, the intergranular corrosion crack in a heat affected zone was observed.

[0062]

[Effect of the Invention] By this invention, it has high temperature strength, a heat-resistant fatigue property, oxidation resistance, outstanding toughness and workability, and outstanding weld zone corrosion resistance compared with the conventional steel of SUH409 grade, and the ferritic stainless steel which was suitable as an automobile exhaust air system member or an exhaust gas path member of

LNG thermal power combined cycle power generation can be offered.

[Translation done.]